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Are $MgCl_2$-Immobilized Single-Center Catalysts for Polyethylene Really Single-Center? Confirmation and Refutation Using Melt Rheometry

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ABSTRACT: Investigation of the melt rheological properties of polyethylenes prepared with chromium, titanium, vanadium, and zirconium catalysts immobilized on $MgCl_2$ supports has confirmed narrow (Schulz−Flory) molecular weight distribution, indicative of single-center catalysis, for Cr-, V-, and Zr-based systems, but not for Ti. In the case of polymers prepared with $MgCl_2$-immobilized Ti complexes and having narrow MWD (M_w/M_n 2−3) according to GPC, deviation from a Schulz−Flory distribution was evident from a decrease in storage modulus with decreasing angular frequencies, whereas polyethylenes prepared with analogous vanadium complexes exhibited a constant (plateau) modulus over a wide frequency range. The presence of the constant plateau modulus in high molecular weight polyethylenes is characteristic for narrow MWD, so that melt rheology provides a valuable tool to prove, or disprove, the presence of a Schulz−Flory distribution in cases where GPC does not provide a definitive answer.

Introduction

Determination of the polydispersity of a polyolefin is routinely carried out using high-temperature gel permeation chromatography (HT-GPC). Relatively broad molecular weight distribution (MWD) is obtained when the catalyst contains a range of different active species, as is generally the case with Ziegler−Natta catalysts, whereas the presence of a single type of catalytically active species should, when chain transfer reactions take place, lead to a narrow (Schulz−Flory) distribution with $M_w/M_n = 2.0$ and $M_z/M_w = 1.5$. In principle, a homogeneous catalyst generating uniform active species should give a polymer with a Schulz−Flory distribution, and this is very often the case. The problem arises when the molecular weight distribution obtained with a catalyst presumed to be single-center deviates from the Schulz−Flory distribution. For example, a M_w/M_n value between 2 and 3 still indicates a narrow molecular weight distribution, but the deviation from the value of 2.0 may be due either to the presence of more than one type of active species, or simply to inaccuracies in the GPC measurement. For heterogeneous catalysts, the possible effects of intraparticle diffusion limitations should also be taken into account.[1] It is generally recognized that molecular weight and polydispersity measurement by HT-GPC is not a simple task, particularly for high molecular weight polymers, and for this reason M_w/M_n values in the range 2−3 are often accepted as being indicative of single-center catalysis.

In recent years, considerable efforts have been made to develop effective approaches for the immobilization of single-center catalysts on suitable supports, the use of heterogeneous or immobilized catalysts being a prerequisite for application of such catalysts in slurry and gas-phase processes for polyolefins.[2] Silica is the most commonly used support material, but there has been increasing interest in the use of magnesium chloride, in view of the established use of $MgCl_2$ as a support for Ziegler−Natta catalysts. Supports of type $MgCl_2/AlR_n(OR')_{3-n}$ have been found to be particularly effective and can be obtained by reaction of AlR_3 with solid or soluble adducts of $MgCl_2$ and an alcohol.[3,4] In previous studies, we and others have used supports of type $MgCl_2/AlEt_n(OEt)_{3-n}$, prepared via the reaction of $AlEt_3$ with solid $MgCl_2$/ethanol adducts, for the immobilization of a range of early and late-transition metal catalysts for ethylene polymerization.[5,6] The molecular weight distributions of the polyethylenes obtained have ranged from narrow ($M_w/M_n = 2$), in the case of immobilized chromium[5d] and vanadium[5e] catalysts, to broad ($M_w/M_n = 4-12$) in the case of bis(imino)pyridyl iron catalysts.[5f]

In addition to GPC, molecular weight distribution can be determined by rheometry, which, in addition to being potentially cheaper and faster, can be applied for polymers that are difficult to dissolve. However, the determination of MWD from rheological measurements is not a simple task. Various mathematical models have been proposed to relate MWD to steady shear viscosity, most of which are based on the tube and reptation theory of de Gennes.[7] Bailly and co-workers have done a considerable amount of simulation work on predicting the viscoelastic moduli of polydisperse entangled melts.[8] Emphasis has also been placed on the development of double reptation models for the rheological determination of MWD.[9−11] In addition, empirical methods have been developed for the characterization of molecular weight distribution. A relatively simple method, in which oscillatory shear behavior is measured as a function of angular frequency, has been described by Zeichner and Patel.[12] In this method, the storage modulus, G', and the loss modulus, G'', are determined. At low frequencies $G'' > G'$, whereas at high frequencies $G' > G''$. The intersection of the modulus vs frequency curves gives the crossover modulus, G_c, which is a measure of the polydispersity of the polymer. The polydispersity index (PI) is derived from the reciprocal of G_c. This method is effective for polyolefins having relatively

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broad MWD, such as polypropylene produced with Ziegler−Natta catalysts,[13] but is less suitable for the high molecular weight, narrow MWD polyethylenes under investigation in the present work.

The rheological behavior of polyethylenes differing in molecular weight and molecular weight distribution has recently been investigated by Vega et al.,[14] who have shown that high molecular weight polyethylene obtained with a metallocene catalyst and having a narrow molecular weight distribution shows a constant ("plateau") modulus over a wide range of angular frequencies. The value of the plateau modulus is dependent on the molecular weight between chain entanglements.[15] In previous studies, we have determined the shear frequency dependence of the storage modulus, G', for polyethylenes prepared using various $MgCl_2$-immobilized catalysts.[5d,f] A constant storage modulus over a wide frequency range was observed for a chromium and a vanadium catalyst, characteristic of polyethylene having narrow MWD and confirming the single-center characteristics of these systems. In contrast, decreases in storage modulus with decreasing frequency were observed for polyethylenes prepared with $TiCl_4$ and with a bis(imino)pyridyl iron catalyst, indicative of broader MWD and the presence of more than one active species.

We have now investigated the viscoelastic response of polyethylenes prepared with a range of transition metal complexes immobilized on $MgCl_2$-based supports, in order to determine the angular frequency dependence of the storage modulus. As indicated above, the presence of a plateau modulus over a wide range of frequency is a characteristic feature of narrow MWD polyethylene, indicating single-center catalysis. The results demonstrate the value of melt rheology in establishing whether or not a polymer has a genuinely narrow, Schulz−Flory MWD as indicated by GPC. It is shown that $MgCl_2$-immobilized titanium complexes, which give polyethylenes with M_w/M_n values in the range 2−3 according to GPC, are actually not single-center catalysts, in contrast to analogous vanadium or zirconium complexes and also chromium-based systems, with which single-center catalyst behavior can be retained after immobilization.

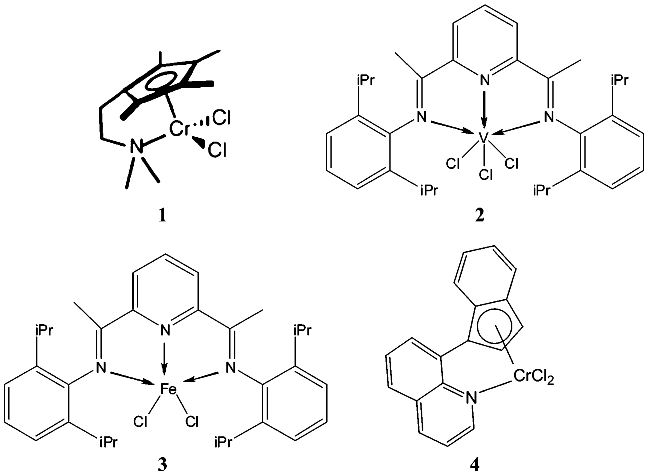
Experimental Section

Materials. All manipulations were performed under an argon atmosphere using glovebox (Braun MB-150 GI or LM-130) and Schlenk techniques. Light petroleum (bp 40−60 °C) and dichloromethane were passed over a column containing Al_2O_3 and stored over 4 Å molecular sieves. All solvents were freeze−thaw degassed twice before use. $AlEt_3$ (1.3 M in heptane) and $Al\textit{i}Bu_3$ (25 wt % in toluene) were obtained from Acros and Akzo Nobel, respectively. Ethylene (3.5 grade supplied by Air Liquide) was purified by passing over columns of BASF RS3-11 supported Cu oxygen scavenger and 4 Å molecular sieves.

Support Preparation and Catalyst Immobilization. Support preparation was performed by the addition of $AlEt_3$ to an adduct $MgCl_2 \cdot 1.1EtOH$ (average particle size d_{50} 82 μm) in light petroleum ($AlEt_3/EtOH = 2$) at 0 °C, after which the mixture was kept at room temperature for 2 days with occasional agitation. The resultant support was washed with light petroleum three times and dried under argon flow and subsequently under vacuum until free-flowing. The Al contents of supports prepared in this way were determined by the H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany. The ethoxide content in each $MgCl_2/AlEt_n(OEt)_{3-n}$ support was determined by gas chromatography (GC) analysis of the ethanol content of a solution obtained by dissolving 50 mg of support in 2.5 mL of BuOH containing a known quantity of PrOH as an internal standard.

Catalyst immobilization was effected by mixing the support (100 mg) with a precatalyst solution in dichloromethane or toluene (1−2 mL, containing 1−4 μmol of precatalyst) and keeping at room temperature or 50 °C overnight. The slurry of the immobilized catalyst was diluted with light petroleum and used directly in ethylene polymerization.

Scheme 1



Polymerization Procedure. Polymerization was carried out in a l L Premex autoclave by charging the immobilized catalyst (100 mg, containing 1−4 μmol precatalyst), slurried in approximately 100 mL of light petroleum, to 400 mL of light petroleum containing the desired amount of cocatalyst, at 50 °C and an ethylene pressure of 5 bar. After catalyst injection, polymerization was continued at constant pressure for 1 h with a stirring rate of 1000 rpm. After venting the reactor, 20 mL of acidified ethanol were added and stirring was continued for 30 min. The polymer was recovered by filtration, washed with water and ethanol, and dried in vacuo overnight at 60 °C.

Polymer Characterization. The polymers were stabilized with 0.2 wt % Irganox 1010 (added as a solution in acetone, after which the polymer was dried in vacuo overnight at 60 °C). Disks of 8 and 25 mm diameter and having a thickness of 0.5 mm were compression molded at 180 °C and 200 bar pressure. Oscillatory shear measurements were performed on an ARES shear rheometer from Rheometric Scientific. Frequency sweep measurements were carried out at 180 °C.

Molecular weights and molecular weight distributions of the polymers were determined by means of gel permeation chromatography on a PL-GPC210 at 135 °C using 1,2,4-trichlorobenzene as solvent. Differential scanning calorimetry (DSC) was carried out with a Q100 differential scanning calorimeter (TA Instruments). The samples (1.5−2.5 mg) were heated to 160 °C at a rate of 10 °C/min for the determination of the first melting temperature (T_{m1}), then cooled down at the same rate to 20 °C. A second heating cycle at 10 °C/min was then applied for the determination of the melting temperature T_{m2}.

Results and Discussion

In previous studies, we have immobilized a wide range of early and late-transition metal catalysts for ethylene polymerization on $MgCl_2/AlR_n(OEt)_{3-n}$ supports. Among the catalysts giving narrow molecular weight distribution polyethylene (M_w/M_n 1.8−2.1, determined by high-temperature GPC) were (η^1:η^5-$Me_2NCH_2CH_2C_5Me_4$)$CrCl_2$ (**1**) and {2,6-[ArN=C(Me)]$_2C_5H_3N$}VCl_3, where Ar = 2,6-diisopropylphenyl (**2**).[5d,f] In contrast, the immobilization of $TiCl_4$ and {2,6-[ArN=C(Me)]$_2C_5H_3N$}$FeCl_2$ (**3**) resulted in broader MWD (M_w/M_n 4.1−5.6). The structures of catalysts **1**−**3** are shown in Scheme 1. In addition to GPC, melt rheometry was used to characterize the molecular weight distributions of these polymers and it was demonstrated that the viscoelastic response of linear polyethylene over a wide range of angular frequency could be used to confirm the

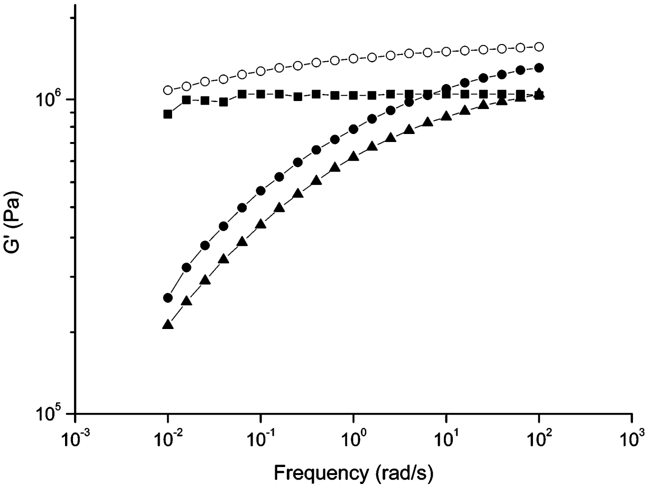


Figure 1. Linear viscoelastic response in oscillatory shear of polyethylene synthesized using catalysts **1** (■), **2** (○), **3** (▲), and $TiCl_4$ (●) (data from ref 5d,f).

differences in MWD indicated by GPC, thereby differentiating between genuinely single-center and multicenter catalysis in these systems. The earlier findings are summarized in Figure 1, in which the polyethylene viscoelastic response is plotted as storage modulus (G') vs angular frequency (ω). Frequency sweep experiments were carried out on polyethylene disks over the frequency range in the viscoelastic regime, which was determined by performing strain tests. The characteristic plateau behavior over the whole frequency range,[14] indicative for samples comprising long chains with similar viscoelastic response and relaxation times (i.e., narrow MWD), is clearly apparent for the polymers synthesized using the chromium and vanadium catalysts **1** and **2** but not for the polymers synthesized with $TiCl_4$ or the iron catalyst **3**. For the latter polymers, the steady decrease in the storage modulus with decreasing frequency is a result of the broader molecular weight distributions, the broadening in the chain length distribution resulting in a broad relaxation time spectrum.

1-(8-Quinolyl)indenylchromium(III) Dichloride. The confirmation that the single-center characteristics of the chromium catalyst **1** were retained after immobilization and activation on a $MgCl_2$-based support prompted us to investigate the immobilization and activation of another chromium complex, [1-(8-quinolyl)indenyl]$CrCl_2$ (**4**), the structure of which is also shown in Scheme 1. This type of complex, containing a rigid spacer group between the cyclopentadienyl ring and the nitrogen atom, has been reported to give improved stability in homogeneous polymerization.[16] Immobilization of this catalyst on $MgCl_2$/$AlEt_n(OEt)_{3-n}$ supports prepared by the reaction of an adduct $MgCl_2 \cdot 1.1EtOH$ with excess $AlEt_3$ was carried out simply by contacting 100 mg of support with 2 mL of dichloromethane containing 1 μmol of **4** at ambient temperature. The results of ethylene polymerizations carried out with either $AlEt_3$ or AliBu$_3$ as cocatalyst and at temperatures in the range 50−70 °C are listed in Table 1. It is apparent that the choice of cocatalyst had a considerable effect on catalyst activity. $AlEt_3$ gave higher activity than AliBu$_3$, but also resulted in a somewhat broader molecular weight distribution. Homogeneous, MAO-activated polymerizations with **4** and related complexes at ambient temperature have been reported to give polydispersities between 2 and 4, and molecular weights in the range 100 000−500 000.[16a] The data in Table 1 reveal that significantly higher molecular weights are obtained after immobilization of the catalyst on a magnesium chloride support, as has been observed for numerous other catalysts.[5] The lower molecular weights obtained in homogeneous polymerization can at least partly be attributed to chain transfer with $AlMe_3$ present in MAO. The results in Table 1 also show that different batches of support, varying in chemical composition, gave different catalyst activities, and that high molecular weight polyethylene was obtained with both $AlEt_3$ and AliBu$_3$. The activities obtained here, and indeed also the activities obtained[5d] with complex **1** on $MgCl_2$/$AlR_n(OEt)_{3-n}$ supports, are higher than those of AlR_3-activated Cr(III) complexes recently claimed[17] to be highly active in comparison with previously reported half-metallocene chromium complexes.

The results of frequency sweep measurements carried out on the polymers prepared under similar conditions but with different cocatalysts (Table 1; entries 1 and 2) are shown in Figure 2. It is evident that the storage modulus of the polymer prepared with AliBu$_3$ as cocatalyst remained constant over the entire frequency range, confirming the narrow molecular weight distribution. In contrast, the sharp drop in G' at lower frequencies for the $AlEt_3$-cocatalyzed sample indicates a broader MWD. This is in line with the GPC results, but it should also be taken into account that the melt rheological properties of polyethylene can be strongly influenced by long-chain branching, even at low levels of branching.[18] Catalysts known to give polyethylenes with significant amounts of long-chain branching include constrained geometry catalysts[19] and certain zirconocenes.[20] Long-chain branching can occur when a vinyl-terminated macromonomer is incorporated into a growing polyethylene chain. C−H bond activation of the polyethylene backbone has also been proposed as a mechanism for the formation of long-chain branching.[21] The presence of long-chain branching can result in the disappearance of the characteristic plateau modulus for narrow MWD polyethylene at lower frequencies.[20d] For a more complete rheological characterization, we therefore also investigated the frequency dependence of the phase angle (G''/G'). Generally, low phase angle values suggest good elastic recovery, whereas higher values are indicative of viscous behavior. Figure 2 shows higher phase angle values for the $AlEt_3$-cocatalyzed sample than for the polymer prepared using AliBu$_3$, indicating a more viscous nature due to a more prominent loss modulus. There is no evidence for any decrease in the phase angle at low frequency, which would be indicative of elastic behavior arising from long-chain branching. Such branching would moreover be expected to give rise to physical network formation and a second, low-frequency plateau for G'; this is also not observed. The DSC data in Table 1 show high melting temperatures (T_{m1} = 142−144 °C) for the nascent polymers and normal melting temperatures (T_{m2} = 131−134 °C) for melt crystallized samples. These observations are typical for linear polyethylene. Though the possibility of long-chain branching cannot be totally ruled out, the degree of branching, if at all present, is too low to have an effect on the crystallization behavior of these polymers.

The GPC data concerning the effect of polymerization temperature on MWD (Table 1; entries 3−5) are less definitive, the value of M_w/M_n increasing from 1.6 at 50 °C to 2.1−2.2 at higher temperatures. Melt rheometry on these samples, however, revealed (Figure 3) a slight deviation of the storage modulus from plateau behavior in the case of the polymers synthesized at 60 and 70 °C, confirming a broadening in the molecular weight distribution. The phase angle profiles show an increase in viscous behavior at low frequencies, indicating the presence of some low molecular weight chains in the polymers synthesized at the higher temperatures.

Table 1. Ethylene Polymerization Using [1-(8-quinolyl)indenyl]CrCl$_2$ (4) on MgCl$_2$-Based Supports[a]

entry	cocatalyst	temp (°C)	activity (kg/mol of Cr•bar•h)	M_w (g/mol)	M_n (g/mol)	M_w/M_n	T_{m1}[d] (°C)	T_{m2}[e] (°C)
1[b]	AlEt$_3$	50	4800	1631 000	544 000	3.0	143.6	133.9
2[b]	Al*i*Bu$_3$	50	2000	1300 000	820 000	1.6	142.4	134.0
3[c]	Al*i*Bu$_3$	50	740	1324 000	824 000	1.6	142.7	133.2
4[c]	Al*i*Bu$_3$	60	900	750 000	338 000	2.2	142.5	131.6
5[c]	Al*i*Bu$_3$	70	1600	850 000	403 000	2.1	143.2	134.0

[a] Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg, AlEt$_3$ or Al*i*Bu$_3$ 1 mmol, ethylene pressure 5 bar, time 1 h. [b] Support composition: MgCl$_2$•0.11AlEt$_{1.72}$(OEt)$_{1.28}$. [c] Support composition: MgCl$_2$•0.13AlEt$_{1.99}$(OEt)$_{1.01}$. [d] Melting temperature from first heating cycle of nascent polymer, as obtained from the reactor. [e] Melting temperature from second heating cycle.

Table 2. Ethylene Polymerization Using Vanadium and Titanium Pincer and Phebox Catalysts on MgCl$_2$-Based Supports[a]

entry	catalyst	temp (°C)	activity (kg/mol of V or Ti•bar•h)	M_w (g/mol)	M_n (g/mol)	M_w/M_n	T_{m1}[e] (°C)	T_{m2}[f] (°C)
1[b]	**9**	50	12 080	926 000	447 000	2.1	143.8	134.7
2[b]	**9**	70	19 920	922 000	462 000	2.0	142.0	134.0
3[c]	**10**	50	11 870	4500 000	1500 000	3.0	141.6	134.0
4[c]	**10**	70	35 400	2200 000	370 000	5.9	141.0	134.9
5[d]	**11**	70	1840	690 000	360 000	1.9	141.4	133.5
6[d]	**12**	50	4590	1406 000	403 000	3.5	142.9	134.9

[a] Polymerization conditions: 500 mL of light petroleum, immobilized catalyst 100 mg, Al*i*Bu$_3$ 1 mmol (entries 3,4,5,6) or 2 mmol (entries 1,2), ethylene pressure 5 bar, time 1 h. [b] Support composition: MgCl$_2$•0.17AlEt$_{2.11}$(OEt)$_{0.89}$. [c] Support composition: MgCl$_2$•0.17AlEt$_{2.25}$(OEt)$_{0.75}$. [d] Support composition: MgCl$_2$•0.21AlEt$_{2.38}$(OEt)$_{0.62}$. [e] Melting temperature from first heating cycle of nascent polymer, as obtained from the reactor. [f] Melting temperature from second heating cycle.

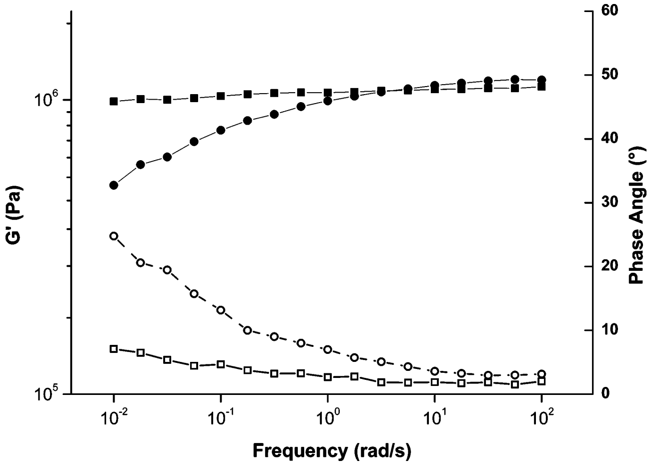


Figure 2. Linear viscoelastic responses in oscillatory shear of polyethylene synthesized using catalyst **4** with Al*i*Bu$_3$ (■, □) and AlEt$_3$ (●, ○) as cocatalyst. Filled symbols represent *G′* and open symbols represent phase angle.

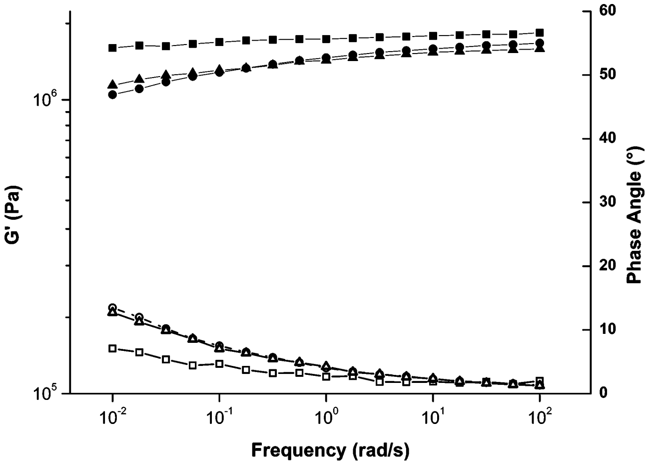


Figure 3. Linear viscoelastic response in oscillatory shear of polyethylene synthesized using catalyst **4** with Al*i*Bu$_3$ as cocatalyst at 50 °C (■), (□), 60 °C (●) (○) and 70 °C (▲), (△). Filled symbols represent *G′* and open symbols represent phase angle.

Titanium and Vanadium Amidinate Complexes. In an earlier publication from our group, the immobilization and activation of vanadium(III) amidinate catalysts on a MgCl$_2$/AlEt$_n$(OEt)$_{3-n}$ support has been reported.[5e] Polyethylene with moderate molecular weight ($M_w \sim 700\,000$) and narrow molecular weight distribution ($M_w/M_n = 2.0$) was obtained. Analogous titanium(III) amidinates gave $M_w \sim 600\,000$ and $M_w/M_n = 2.3$. It was concluded, on the basis of these narrow molecular weight distributions, that the single-center behavior of these catalysts was retained after immobilization on the support. However, the increase in the value of M_w/M_n on going from vanadium to titanium, albeit slight, raises some doubt concerning the single-center nature of the titanium-based systems. In order to resolve this question, the melt rheological properties of these polymers have now been investigated. The structures of the amidinate catalysts, first prepared by Hessen and co-workers,[22] are shown in Scheme 2. Polymerization was carried out at 50 °C, using Al*i*Bu$_3$ as cocatalyst.[5e] The results of frequency sweep tests carried out on the polymers prepared with [Me$_3$SiNC(Ph)NCH$_2$CH$_2$NMe$_2$]MCl$_2$(THF), where M = V (**5**) or Ti (**6**), are shown in Figure 4. A very slight decrease in storage modulus with decreasing frequency is apparent for the vanadium-catalyzed polymer, whereas a much steeper decrease in *G′* is observed for the polymer prepared with the titanium complex **6**. Similar differences between vanadium and titanium are evident from Figure 5, which shows the results obtained with polymers prepared with [PhC(NSiMe$_3$)$_2$]MCl$_2$(THF)$_2$, where M = V (**7**) or Ti (**8**). The phase angle behavior also confirms the less viscous nature of the vanadium-catalyzed polymers. These results provided a first indication of a much stronger deviation from single-center behavior in the case of MgCl$_2$-immobilized titanium catalysts than for vanadium catalysts with the same ligand structure and prompted us to investigate and compare other titanium- and vanadium-based systems.

Titanium and Vanadium Pincer and Phebox Complexes. In recent years, many advances have been made in the synthesis and development of nonmetallocene single-center catalysts for olefin polymerization.[23,24] Much attention has been given to NNN-pincer type complexes, as a result of both their catalytic properties and ease of synthesis. Much less work has been carried out on NCN-pincer complexes containing a *σ*-aryl donor

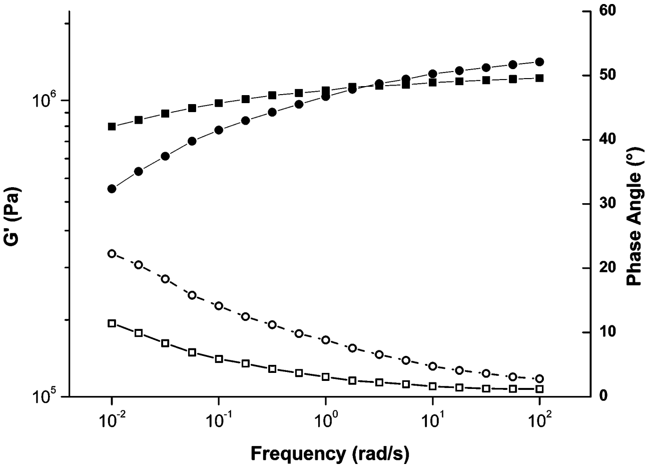


Figure 4. Linear viscoelastic response in oscillatory shear of polyethylene synthesized using catalysts **5** (■, □) and **6** (●, ○). Filled symbols represent G' and open symbols represent phase angle.

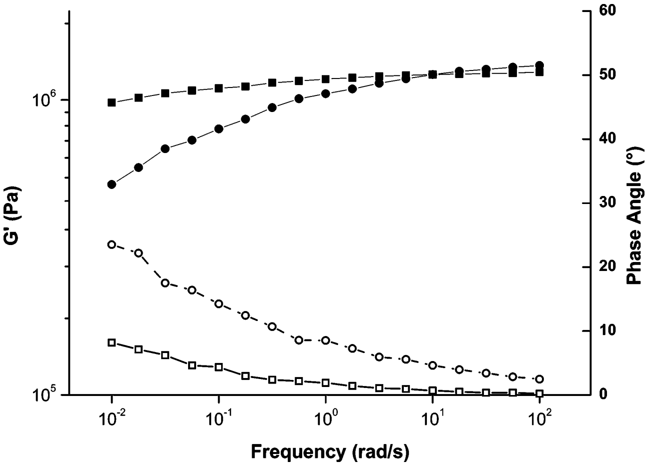
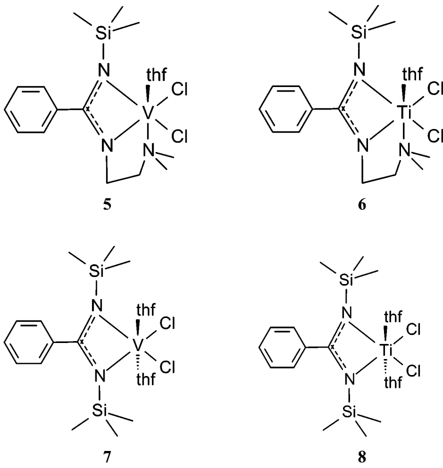


Figure 5. Linear viscoelastic response in oscillatory shear of polyethylene synthesized using catalysts **7** (■, □) and **8** (●, ○). Filled symbols represent G' and open symbols represent phase angle.

Scheme 2



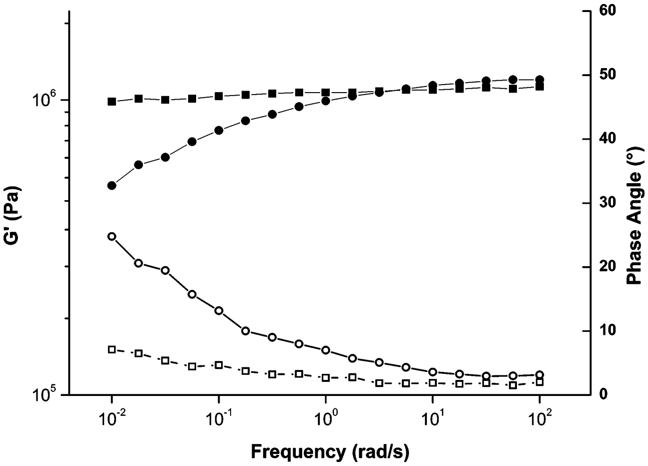


Figure 6. Linear viscoelastic response in oscillatory shear of polyethylene synthesized at 50 °C using vanadium (■, □) and titanium (●, ○) pincer complexes **9** and **10** (Table 2; entries 1 and 3). Filled symbols represent G' and open symbols represent phase angle.

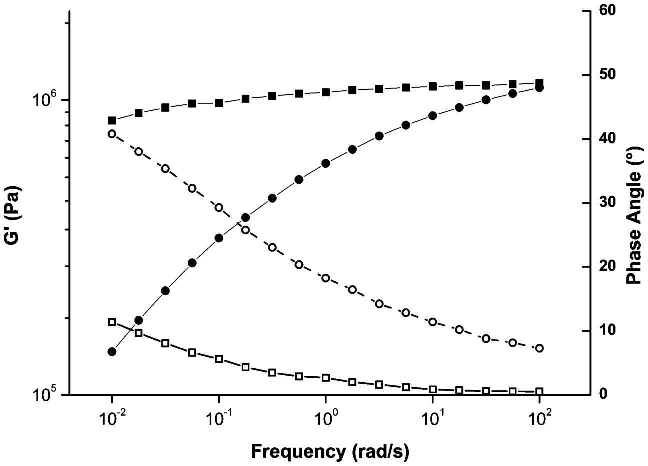


Figure 7. Linear viscoelastic response in oscillatory shear of polyethylene synthesized at 70 °C using vanadium (■, □) and titanium (●, ○) pincer complexes **9** and **10** (Table 2; entries 2 and 4). Filled symbols represent G' and open symbols represent phase angle.

ligand.[25] Recently, a series of pincer complexes, including the vanadium and titanium complexes **9** and **10**, has been synthesized and tested in ethylene polymerization. Full details of the synthesis and crystal structures of these complexes will be reported elsewhere.[26] It has been found that, whereas these and related complexes[25b] give low activity and poor stability under homogeneous polymerization conditions, using MAO as activator, very high activities can be obtained after immobilization on magnesium chloride. The results of polymerizations with complexes **9** and **10**, immobilized on $MgCl_2/AlEt_n(OEt)_{3-n}$ supports, are given in Table 2. Immobilization was carried out by contacting 100 mg of support with a solution of the pincer catalyst (1 μmol) in toluene (1 mL) at ambient temperature overnight. Stable polymerization activities were observed at both 50 and 70 °C, yielding activities of up to around 20000 and 35000 kg/mol•bar•h with complexes **9** and **10**, respectively. The titanium pincer catalyst **10** gave very high molecular weight polyethylene, but the polydispersity values in Table 2 indicate a significant deviation from a Schulz−Flory distribution, particularly for polymerization at 70 °C. In contrast, the vanadium pincer catalyst **9** gave narrow distribution irrespective of the polymerization temperature, indicating retention of single-center behavior. This was confirmed by determination of the melt rheological properties of these polymers, the results of which are shown in Figures 6 and 7. The vanadium-catalyzed polymers show almost constant values of G' over the entire frequency range, although there was a slight deviation for the polymer synthesized at 70 °C, whereas the polymers prepared with the analogous titanium complex exhibit strong decreases in G' with decreasing frequency.

A further comparison between vanadium- and titanium-based systems was made with complexes **11** and **12** (Scheme 3)

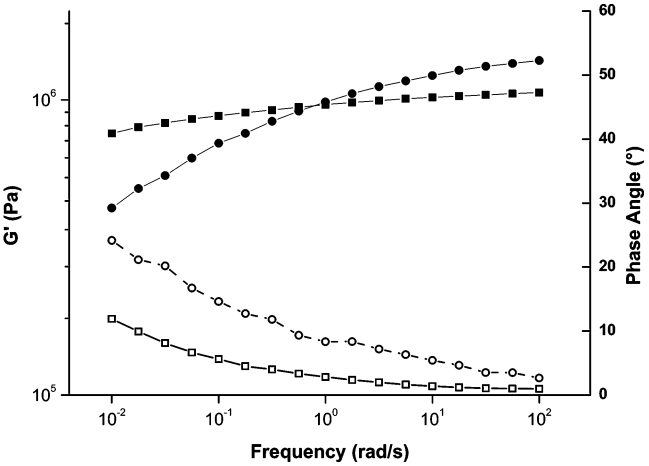
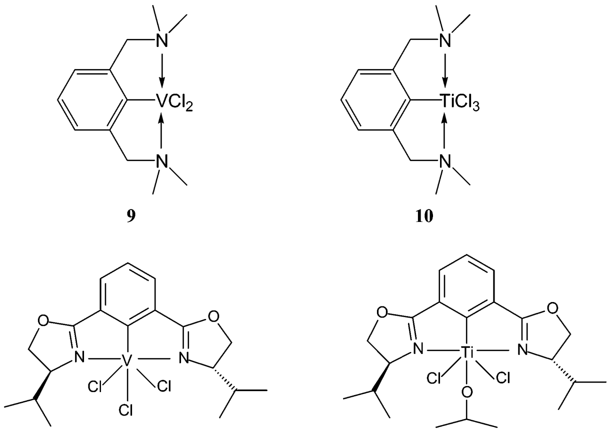


Figure 8. Linear viscoelastic response in oscillatory shear of polyethylene synthesized using vanadium (■, □) and titanium (●, ○) phebox complexes **11** and **12** (Table 2; entries 5 and 6). Filled symbols represent *G*′ and open symbols represent phase angle.

Scheme 3



containing the 2,6-bis(2′-oxazolinyl)phenyl (phebox) ligand. These complexes, like the pincer complexes **9** and **10**, were synthesized by Chuchuryukin et al.[26] via transmetallation reactions involving arylgold(1) phosphine precursors.[27] In MAO-activated homogeneous polymerization in toluene at 50 °C, the activity of the vanadium phebox complex **11** decayed rapidly, the overall activity being only around 70 kg/mol•bar•h.[26] No activity was observed with the titanium complex **12**. However, both of these phebox complexes were active when immobilized on magnesium chloride supports. Immobilization was carried out in toluene at 50 °C, at loadings of 2 and 4 μmol/100 mg support for **11** and **12**, respectively. The GPC data in Table 2 (entries 5 and 6) and the melt rheological behavior (Figure 8) of polymers prepared with the immobilized complexes reveal, once more, a fundamental difference between vanadium and titanium, narrow MWD being obtained with the vanadium complex **11**, but not with the related titanium complex **12**. In Figure 8, it is apparent that the plateau modulus of vanadium catalyzed polymer is lower than the characteristic value of 2 MPa. It is well-known that this lowering in plateau modulus can be caused by shrinkage in the sample, which occurs when the stresses in the sample are released in the molten state. In a measurement on a parallel plate rheometer in dynamic mode, the stress constant is related to the third power of the sample radius. Shrinkage of the sample can therefore have a strong effect on the determination of the true plateau modulus.

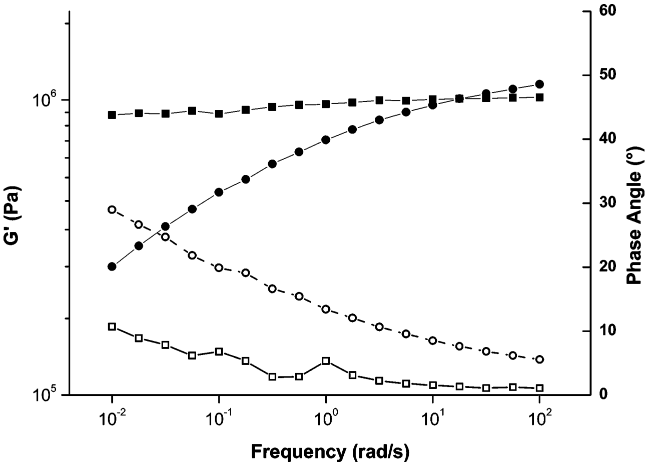


Figure 9. Linear viscoelastic response in oscillatory shear of polyethylene synthesized using Cp_2ZrCl_2 (■, □) and Cp_2TiCl_2 (●, ○). Filled symbols represent *G*′ and open symbols represent phase angle.

Titanocene and Zirconocene-Based Systems. In earlier studies on the immobilization of single-center catalysts on $MgCl_2/AlEt_n(OEt)_{3-n}$ supports, we have investigated the metallocenes Cp_2TiCl_2 and Cp_2ZrCl_2, as well as $CpTiCl_3$ and related half-titanocene complexes.[5a,b] GPC analysis of the resulting polyethylenes indicated narrow polydispersities, with M_w/M_n values mostly in the range 2−3, and it was concluded that this was an indication that the single-center characteristics of these catalysts were retained after immobilization on the support. However, the deviation from single-center behavior exhibited by the titanium amidinate, pincer and phebox complexes described above, apparent from the polymer melt rheological properties, prompted us to carry out similar frequency sweep experiments on titanocene- and zirconcene-based systems to ascertain which of these may genuinely be classified as single-center. A polyethylene prepared[5b] with Cp_2TiCl_2 had an M_w of 1 633 000 and $M_w/M_n = 2.9$, while Cp_2ZrCl_2 gave[5a] an M_w of 896 600 and $M_w/M_n = 2.7$. Figure 9 shows the frequency dependence of *G*′ for polymers prepared with these complexes. It is evident that the single-center behavior of the zirconocene is retained after immobilization on a $MgCl_2/AlEt_n(OEt)_{3-n}$ support, whereas this is not so for the titanocene. The melt rheological properties of the polymers prepared[5b] with the $MgCl_2$-immobilized half-titanocene complexes are illustrated in Figure 10, which in each case clearly shows significant decreases in *G*′ with decreasing frequency. In other words, these results deviate from the rheological behavior expected for polymers having narrow (Schulz−Flory) MWD. The narrow molecular weight distributions (M_w/M_n 2.0−2.5) determined[5b] using GPC can therefore not be taken as reliable proof of single-center catalysis in these systems.

The results obtained with the $MgCl_2$-supported titanium catalysts, in contrast to those of analogous vanadium and zirconium complexes, indicate the formation of more than one type of active species. A physical explanation for deviation from a pure Schulz−Flory distribution, such as nonuniform monomer concentration within the growing polymer particle, can be discounted, as this would not depend on a particular transition metal. One possibility for the formation of multiple active species could involve a disproportionation of $CpTiCl_3$, and analogous half-titanocenes, on the support surface, forming Cp_2TiCl_2 and $TiCl_4$. Immobilization of $TiCl_4$ itself on a $MgCl_2/AlEt_n(OEt)_{3-n}$ support leads to a Ziegler−Natta type catalyst with high activity and giving relatively broad molecular weight distribution.[5b] The sensitivity of polymer melt rheology to long-

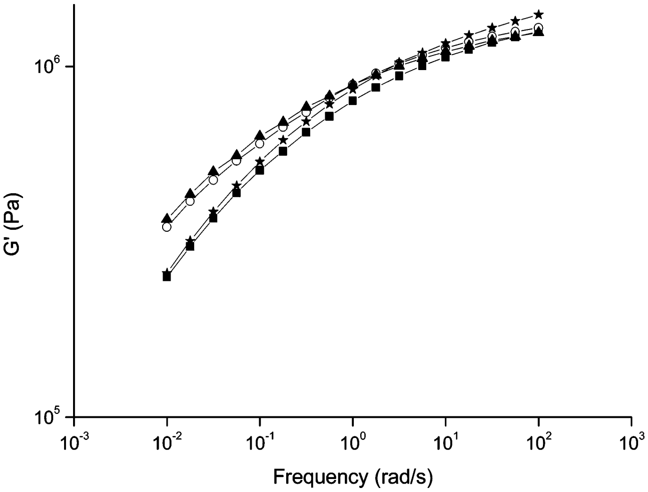


Figure 10. Linear viscoelastic response in oscillatory shear of polyethylene synthesized using (PhCMe$_2$Cp)TiCl$_3$ (○), (Indenyl)TiCl$_3$ (■), (*t*BuCp)TiCl$_3$ (▲), and (*t*Bu$_3$P═N)CpTiCl$_2$ (★).

chain branching is such that this, like the presence of multiple active species, may affect the angular frequency dependence of the storage modulus. However, no indications were obtained for the presence of long-chain branching in the polyethylenes investigated in the present study.

Conclusions

Melt rheometry is a valuable diagnostic tool to determine the presence, or absence, of a narrow, Schulz−Flory molecular weight distribution in polyethylene. A low sensitivity of the storage modulus, G', to changes in angular frequency gives a plateau modulus characteristic of narrow MWD polyethylene, whereas a decrease in G' with decreasing frequency is indicative of a broadening of the molecular weight distribution. The method is particularly useful in cases where GPC data indicate narrow polydispersity, but where the ratio M_w/M_n differs from the Schulz−Flory value of 2.0, taking into account the experimental difficulties associated with GPC analysis of high molecular weight polymers and the fact that measured M_w/M_n values in the range 2−3 are often taken to be close enough to 2 to be indicative of the presence of a single type of active species in polymerization.

Application of the method to polyethylenes prepared with a range of early transition metal complexes on MgCl$_2$-based supports reveals that the retention of single-center behavior of the catalyst after immobilization on the support is dependent on the transition metal. A constant storage modulus over a wide range of angular frequencies, consistent with a Schulz−Flory MWD, was observed for polyethylenes prepared with MgCl$_2$-immobilized chromium, vanadium and zirconium complexes, confirming that in these systems the single-center characteristics of the catalyst can be retained after immobilization and activation on the support. In contrast, significant decreases in G' with decreasing frequency were observed for the polymers prepared with MgCl$_2$-immobilized titanium complexes, indicating a broadening in molecular weight distribution and the presence of more than one active species. The previous assumptions of single-center catalysis in the case of the Ti-based systems, based on GPC, can therefore be discounted. The finding that immobilization on magnesium chloride of vanadium and titanium complexes having similar ligand structures leads to retention of single-center behavior in the case of vanadium but not with titanium indicates that high-activity vanadium-based systems are particularly interesting candidates for the synthesis of polyethylene homo- and copolymers with narrow composition distribution.

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References and Notes

(1) Floyd, S.; Heiskanen, T.; Taylor, T. W.; Mann, G. E.; Ray, W. H. *J. Appl. Polym. Sci.* **1987**, *33*, 1021−1065.

(2) (a) Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347−1376. (b) Severn, J. R.; Chadwick, J. C.; Duchateau, R.; Friederichs, N. *Chem. Rev.* **2005**, *105*, 4073−4147.

(3) Sacchetti, M.; Pasquali, S.; Govoni, G. US 5,698,487.

(4) Nakayama, Y.; Bando, H.; Sonobe, Y.; Kaneko, H.; Kashiwa, N.; Fujita, T. *J. Catal.* **2003**, *215*, 171−175. (b) Nakayama, Y.; Bando, H.; Sonobe, Y.; Suzuki, Y.; Fujita, T. *Chem. Lett. (Jpn.)* **2003**, *32*, 766−767. (c) Nakayama, Y.; Bando, H.; Sonobe, Y.; Fujita, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 617−625. (d) Nakayama, Y.; Bando, H.; Sonobe, Y.; Fujita, T. *J. Mol. Catal. A: Chem.* **2004**, *213*, 141−150.

(5) (a) Severn, J. R.; Chadwick, J. C. *Macromol. Rapid Commun.* **2004**, *25*, 1024−1028. (b) Severn, J. R.; Chadwick, J. C. *Macromol. Chem. Phys.* **2004**, *205*, 1987−1994. (c) Severn, J. R.; Chadwick, J. C.; Van Axel Castelli, V. *Macromolecules* **2004**, *37*, 6258−6259. (d) Severn, J. R.; Kukalyekar, N.; Rastogi, S.; Chadwick, J. C. *Macromol. Rapid Commun.* **2005**, *26*, 150−154. (e) Severn, J. R.; Duchateau, R.; Chadwick, J. C. *Polym. Int.* **2005**, *54*, 837−841. (f) Huang, R.; Kukalyekar, N.; Koning, C. E.; Chadwick, J. C. *J. Mol. Catal. A: Chem.* **2006**, *260*, 135−143.

(6) (a) Huang, R.; Liu, D.; Wang, S.; Mao, B. *Macromol. Chem. Phys.* **2004**, *205*, 966−972. (b) Huang, R.; Liu, D.; Wang, S.; Mao, B. *J. Mol. Catal. A: Chem.* **2005**, *233*, 91−97. (c) Xu, R.; Liu, D.; Wang, S.; Mao, B. *Macromol. Chem. Phys.* **2006**, *207*, 779−786.

(7) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*, Clarendon, Oxford, U.K., 1986.

(8) (a) Leygue, A.; Bailly, C.; Keunings, R. *J. Non-Newtonian Fluid Mech.* **2006**, *133*, 28−34. (b) Liu, C.; He, J.; Keunings, R.; Bailly, C. *Macromolecules* **2006**, *39*, 3093−3097. (c) Liu, C.-Y.; Keunings, R.; Bailly, C. *Macromolecules* **2007**, *40*, 2946−2954.

(9) des Cloizeaux, J. *Macromolecules* **1990**, *23*, 4678−4687.

(10) Mead, D. W. *J. Rheol.* **1994**, *38*, 1797−1827.

(11) Guzman, J. D.; Schieber, J. D.; Pollard, R. *Rheol. Acta.* **2005**, *44*, 342−351.

(12) Zeichner, G. R.; Patel, P. D. *Proc. 2nd World Congr. Chem. Eng.* **1981**, *6*, 333−337.

(13) Chadwick, J. C.; van der Burgt, F. P. T. J.; Rastogi, S.; Busico, V.; Cipullo, R.; Talarico, G.; Heere, J. J. R. *Macromolecules* **2004**, *37*, 9722−9727.

(14) Vega, J. F.; Rastogi, S.; Peters, G. W. M.; Meijer, H. E. H. *J. Rheol.* **2004**, *48*, 663−678.

(15) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.

(16) (a) Enders, M.; Fernández, P.; Ludwig, G.; Pritzkow, H. *Organometallics* **2001**, *20*, 5005−5007. (b) Mihan, S.; Lilge, D.; De Lange, P; Schweier, G.; Schneider, M.; Rief, U.; Handrich, U.; Hack, J.; Enders, M.; Ludwig, G.; Rudolph, R. US 6,699,948. (c) Enders, M. *Macromol. Symp.* **2006**, *236*, 38−47.

(17) Xu, T.; Mu, Y.; Gao, W.; Ni, J.; Ye, L.; Tao, Y. *J. Am. Chem. Soc.* **2007**, *127*, 2236−2237.

(18) (a) Bersted, B. H. *J. Appl. Polym. Sci.* **1985**, *30*, 3751−3765. (b) Shroff, R. N.; Mavridis, H. *Macromolecules* **1999**, *32*, 8454−8464. (c) Wood-Adams, P. A.; Dealy, J. M.; deGroot, A. W.; Redwine, O. D. *Macromolecules* **2000**, *33*, 7489−7499. (d) Doerpinghaus, P. J.; Baird, D. G. *J. Rheol.* **2003**, *47*, 717−736. (e) van Ruymbeke, E.; Stéphenne, V.; Daost, D.; Godard, P.; Keunings, R.; Bailly, C. *J. Rheol.* **2005**, *49*, 1503−1520. (f) Stadler, F. J.; Piel, C.; Kaminsky, W.; Münstedt. H. *Macromol. Symp.* **2006**, *236*, 209−218.

(19) Lai, S.-Y.; Wilson, J. R.; Knight, G. W.; Stevens, J. C.; Chum, P.-W. S. US 5,272,236.

(20) (a) Malmberg, A.; Kokko, E.; Lehmus, P.; Löfgren, B.; Seppälä, J. V. *Macromolecules* **1998**, *31*, 8448−8454. (b) Harrison, D.; Coulter, I. M.; Wang, S.; Nistala, S.; Kuntz, B. A.; Pigeon, M.; Tian, J.; Collins, S. *J. Mol. Catal. A: Chem.* **1998**, *128*, 65−77. (c) Kolodka, E.; Wang, W.-J.; Charpentier, P. A.; Zhu, S.; Hamielec, A. E. *Polymer* **2000**,

41, 3985−3991. (d) Gabriel, C.; Kokko, E.; Löfgren, B.; Seppälä, J. V.; Münstedt. H. *Polymer* **2002**, *43*, 6383−6390. (e) Piel, C.; Stadler, F. J.; Kaschta, J.; Rulhoff, S.; Münstedt, H.; Kaminsky, W. *Macromol Chem. Phys.* **2006**, *207*, 26−38.

(21) Reinking, M. K.; Orf, G.; McFaddin, D. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2889−2898.

(22) Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Eur. J. Inorg. Chem.* **1998**, 1867−1870.

(23) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283−315.

(24) Resconi, L.; Chadwick, J. C.; Cavallo, L. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Oxford, U.K., 2006; Vol. 4, pp 1005−1166.

(25) (a) Donkervoort, J. G.; Jastrzebski, J. T. B. H.; Deelman, B.-J.; Kooijman, H.; Veldman, N.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 4174−4184. (b) Matsunaga, P. T. WO 99/57159.

(26) Chuchuryukin, A. V.; Huang, R.; van Faassen, E. E.; van Klink, G. P. M.; Lutz, M.; Chadwick, J. C.; Spek, A. L.; van Koten, G. Manuscript in preparation.

(27) Contel, M.; Stol, M.; Casado, M. A.; van Klink, G. P. M.; Ellis, D. D.; Spek, A. L.; van Koten, G. *Organometallics* **2002**, *21*, 4556−4559.

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